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Chemical-physical Analysis on the Stele from the Heated Stone Structures of S. Andrea in Travo (PC): Preliminary Results.

Vittoria Guglielmi[1], Valeria Comite[1], Claudia Asia Pini[1], Chiara Andrea Lombardi[1], Maria Bernabò Brea[3], Alain Beeching[4], Sara Pescio[2], Luca Trombino[2], Paola Fermo[1]

[1] *Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, Milano, Italy;* vittoria.guglielmi@unimi.it, paola.fermo@unimi.it, valeria.comite@unimi.it

[2] *Dipartimento di Scienze della Terra "Ardito Desio", Università degli Studi di Milano, MI, Italy;* luca.trombino@unimi.it, sara.pescio@unimi.it

[3] *Ispettore Onorario Soprintendenza ABAP Parma e Piacenza, Parma, Italy.;* mbbrea@libero.it

[4] *Université Lumière-Lyon 2, UMR Archéorient, Maison de l'Orient et de la Méditerranée, Lyon* alain.beeching@gmail.com

***Abstract* – In the 1980s, in the locality of S. Andrea a Travo (Piacenza), a Neolithic settlement, datable between 4300 and 3800 B.C., was found, which represents one of the most important sites in northern Italy in terms of dwellings and structures. In the area furthest from the river and the houses, there were 23 hearths with burnt stones, which, according to chemical analyses, were used for cooking meat. However, a number of slabs were also found in the hearths with shapes and features that suggest rough anthropomorphic stelae; in particular, the one with dark traces is the main focus of this work. By analysing a fragment of one of the main stelae through electron microscopy coupled with X-ray fluorescence and vibrational spectroscopy, the present study aims to verify the reliable hypothesis that the stelae were decorated with colour, confirming that the culinary function of the hearths was linked to social events, in which the stelae had some ritual and symbolic value.**

I. INTRODUCTION

From the Neolithic site of S. Andrea at Travo, on a river terrace in the middle of the Trebbia Valley (Piacenza) [1, 2], a number of stelae have come to light, consisting of slabs made of sandstone and limestone bearing traces of workmanship by light hammering. One of them, 50 cm high, is clearly anthropomorphic; in another, the triangular-ogival shape of the upper part seems to be underlined by brown bands that could be intentional (fig. 1) [3].

The site of S. Andrea, dated to between 4300 and 3800 B.C., belongs to the cultural period called 'Recent Emilian Neolithic' [4], in which influences from several areas converge. A number of rectangular buildings arranged along the riverbank and 23 hearths clustered upstream of the houses were brought to light at the site. The hearths are of the 'burnt pebble' type formed by shallow sub-rectangular pits, filled with coals covered with pebbles of various lithologies, that were taken from the nearby Trebbia riverbed [3].

Four hearths contained, in addition to pebbles, both fragments of stelae and complete but intentionally fragmented stelae, as the impact traces reveal. Pits and lithic fillings show traces of heating, which the thermometric study indicates was between 350° and 450° Celsius [5]; sedimentological and geochemical analyses suggest their probable use was for cooking meat [6].

However, archaeological data indicates that these are not structures for everyday use. The possible interpretation is that they are culinary structures intended for collective social ceremonies; the intentionally fragmented stelae, which evoke human figures, testify to a ritual gesture. The small stelae of Travo are the oldest anthropomorphic stelae in Italy; some comparisons have been made with stelae coming from funerary contexts in France and Austria [3, 7, 8], also sometimes showing traces of colour.

Therefore, it is of primary importance to ascertain the exact nature, and possibly the intentionality, of the brown traces observed in some of the Travo stelae.

In fact, knowing the nature of materials utilised in artworks, could be a further step to better contextualise them and give some additional clues to archaeologists' research. In particular, the black areas of the stele in figure 1 were investigated in order to reveal whether or not a pigment (and in a positive finding, which one) was present on the stele's surface.

The identification of pigments, and possibly binders, can be a way to have important information about the availability of raw materials, as well as the technological knowledge to prepare pigments. In this preliminary work, Scanning Electron Microscopy equipped with an Energy Dispersive X-ray Spectroscopy (SEM-EDXS) and in situ Raman spectroscopy have been applied. These techniques are indeed commonly used in the field of cultural heritage for the characterisation of painting materials present in different kinds of works of art [9-23] and they were applied directly on the surface.

The research outlined some interesting first results about the chemical composition of the dark traces, such as the presence of carbon black and possibly iron-based minerals. The outcomes will be presented and discussed in the scope of the unique context in which they were found.

II. MATERIALS AND METHODS

A. The stele

The stele was found in the rectangular hearth US 272, overlaid on another one. Above the hearths there were 180 stones, irregularly distributed. Among them there were also four slabs, two of which were fragmented but connected.

The examined samples belong to a fine, micaceous sandstone stele, 20x21x3.5-4 cm, triangular-ogival in shape, and broken into 10 connected pieces, laying in the hearth, but missing a small side part. Its shape is natural but modified by hammering and abrasion. One face shows a few traces of dark-brown colour (Fig. 1).

B. Analytical techniques

The SEM-EDXS examinations were performed by a Hitachi TM4000 scanning electron microscope equipped with a 4-quadrant BSE detector, a low-vacuum S.E. detector and Oxford AztecOne EDX system and, as the analyses were carried out in low vacuum conditions, no coating application was required [14, 24]. Moreover, the selected sample (Fig. 1b) was small enough to be analysed by the SEM-EDXS benchtop instrumentation without any sampling. SEM-EDXS analyses were performed on dark and light areas, respectively indicated by black and white arrows (Fig. 1b).

With regard to elemental analyses, the measurements were performed on surface areas of about 4x3 mm and were repeated three times slightly moving the probe to different position for each repetition.

Raman analyses were performed by a BWTek i-Raman EX portable instrument, equipped with a fibre optic probe and the source was an Nd-YAG laser emitting at 1064 nm. The Raman measurements were performed directly on the sherds, with no sampling [25, 26]; all the spectra were obtained as an average of 80 scans in the spectral range of 200-2500 cm^{-1}. The identification of the different substances was made by comparing the spectra obtained on samples with the ones present in the literature [27, 28].

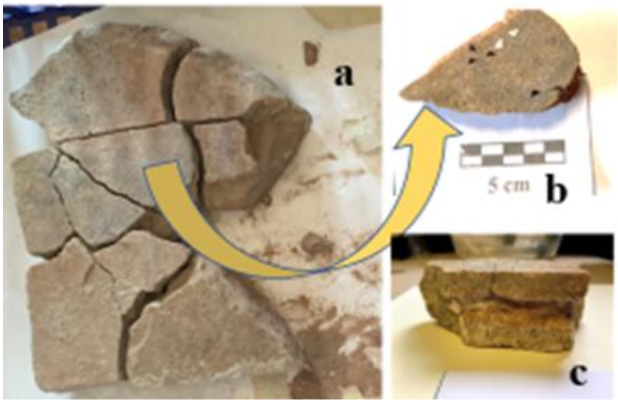

Fig. 1. a) The fragmented and incomplete small stele of Travo; b) the fragment analysed by SEM-EDX; c) the stele seen in cross-section.

III. RESULTS AND DISCUSSION

The morphology of the two areas was really similar, so no particular observations could be done.

Both dark and light areas were predominantly characterised by carbon, oxygen, aluminium, silicon, calcium, and iron, whereas potassium, magnesium, titanium, sodium, sulphur, phosphorus, and chlorine were present as trace elements. Tables 1 and 2 show the results of the semi-quantitative chemical analyses obtained respectively on the dark and light areas.

The most interesting results came out of the comparison between the percentages of the main elements, in particular, carbon, calcium and iron. The former is just slightly predominant on the dark area and this observation, by itself, could lead one to think that its presence is not related to the area's colour. However, one must consider that carbon may be present as carbonate as well as native carbon. Taking into account that the average percentage of calcium on the white areas is almost 50% higher, the hypothesis that carbon is higher in percentage as carbon black (and subsequently lower in percentage as calcium carbonate) on dark areas and vice versa on light areas seems consistent.

It is also to be considered that the average percentage of iron on the dark areas is about 4,5%, whereas it is under 3% on lighter areas. Since iron oxides can also display as a dark brown colour, another possible conjecture was that the dark colour was related to the presence of black iron oxide [29]. What has been evinced through the comparison of elements' percentages, looks to be reinforced by the comparison of the EDX spectra shown in Fig.2, respectively obtained on a dark area (red line) and a light area (yellow line), since the peak of calcium on the light area is evidently higher than in the dark area and the opposite verifies for carbon and iron on the dark area.

Table 1. Results of the SEM-EDX semi-quantitative analyses on the dark areas

Element	W% area 1	W% area 2	W% area 3	W% average
C	31,29	28,82	27,27	29,13
O	41,09	43,34	43,86	42,76
Al	4,49	5,01	4,55	4,68
Si	11,29	12,91	13,66	12,62
K	1,25	1,15	1,29	1,23
Ca	4,48	3,16	3,8	3,81
Fe	4,65	4,01	4,16	4,27
Mg	0,87	0,87	0,73	0,82
Ti	0,29	0,29	0,27	0,28
Na	-	0,14	0,15	0,15
S	0,14	0,14	0,13	0,14
P	0,16	0,12	0,11	0,13
Cl	0.00	0,06	0,04	0,05

Table 2. Results of the SEM-EDX semi-quantitative analyses on the light areas

Element	W% area 1	W% area 2	W% area 3	W% average
C	27,87	29,39	27,83	28,36
O	42,88	43,22	44,44	43,51
Al	4,06	4,07	3,58	3,90
Si	11,25	13,01	12,46	12,24
K	1,11	0,96	0,88	0,98
Ca	8,38	4,85	6,53	6,59
Fe	3,05	3,03	2,9	2,99
Mg	0,72	0,69	0,65	0,69
Ti	0,26	0,27	0,23	0,25
Na	0,16	0,22	0,25	0,21
S	0,15	0,15	0,14	0,15
P	-	0.09	0,09	0,09
Cl	0.00	0,07	0,05	0,06

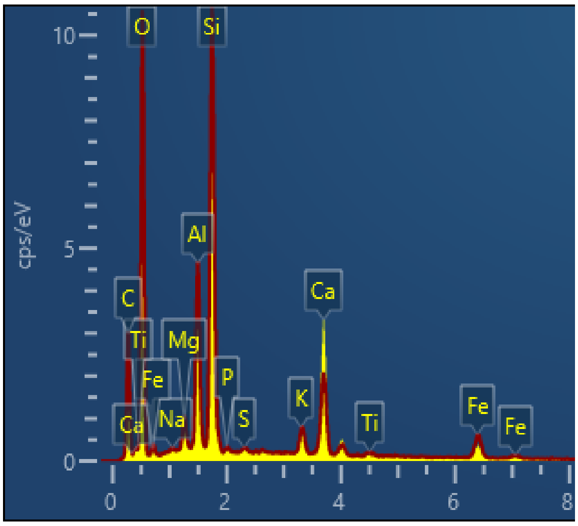

Fig. 2. EDX spectra obtained on a dark area (area 1 of table 1, red line) and a light area (yellow line).

Raman analyses were performed on plenty of areas, not only on the sample in Fig.1, but also on the other fragments of the stele. All the spectra were characterised by an intense fluorescence background and by the widespread presence of calcite (bands at 1086, 711 and 286 cm^{-1} [26]), quartz (467 cm^{-1} [30]) and K-feldspar (513 cm^{-1} [31]). In one case, on an area on the interface between a dark and a light area, a spectrum where fluorescence was less interfering was obtained, clearly showing the unmistakable bands of carbon black at about 1590 and 1300 cm^{-1} [32, 33], other than the so-called D4 weak band at 1165 cm^{-1} [34]. A high peak at 1086 cm^{-1} was also present, which could probably be attributed to calcite, but it is not to exclude *a priori* that it could be due to siderite [35]. These results corroborated the hypothesis that the black colour was, perhaps just partially, related to the presence of carbon black.

IV. CONCLUSIONS

The main notable outcome of the investigation was the identification of the composition of the black areas on the stele. The presence of carbon black on the analysed dark surfaces was undoubtedly recognised by Raman spectroscopy. It is worth noting that both Raman and SEM-EDX analyses give rise to the hypothesis of the presence of an iron-based substance too, possibly siderite. Moreover, the presence of manganese or iron/manganese oxides, which, together with charcoal were some of the most commonly used pigments in antiquity for black paintings, were definitely excluded [36]. The good results obtained with this first and totally non-destructive approach, encouraged to proceed with the study by means of micro-destructive techniques, such as XRD, FTIR, in order to go more in depth in the mineralogical composition of all the different parts of the stele, namely the top, middle, and bottom. Moreover, an extraction procedure of some micro-samples will be performed, followed by a GC-MS analysis, with the aim of verifying the possible presence of organic materials, enhancing the chemical data set on the oldest neolithic Italian stele.

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